



(11) Publication number: **0 453 237 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **91303379.1**

(51) Int. Cl.<sup>5</sup>: **G03F 7/037**

(22) Date of filing: **16.04.91**

(30) Priority: **16.04.90 JP 99788/90**  
**19.10.90 JP 279088/90**

(43) Date of publication of application:  
**23.10.91 Bulletin 91/43**

(84) Designated Contracting States:  
**DE FR GB**

(71) Applicant: **FUJITSU LIMITED**  
**1015, Kamikodanaka Nakahara-ku**  
**Kawasaki-shi Kanagawa 211 (JP)**

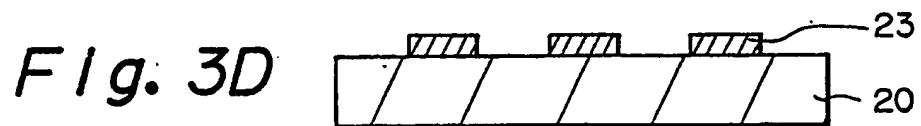
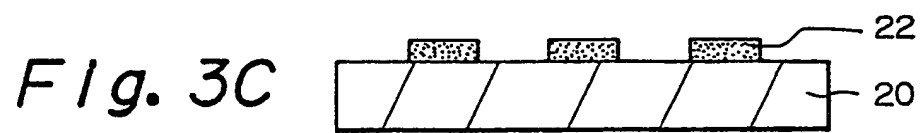
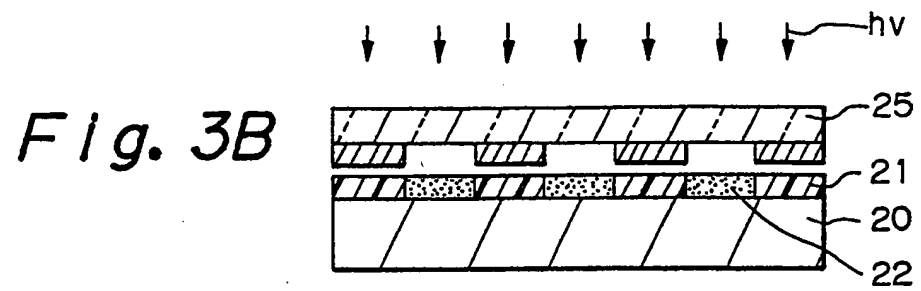
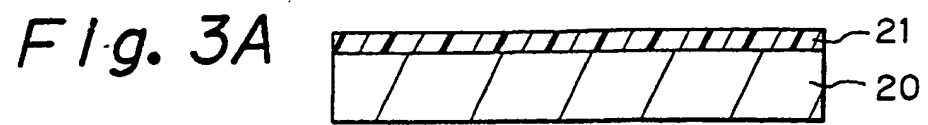
(72) Inventor: **Tani, Motoaki**  
**Berumezon 512, 16-20, Sakae-cho 1-chome**  
**Atsugi-shi, Kanagawa 243 (JP)**  
Inventor: **Horikoshi, Eiiji**  
**3-6, Hachimandai 1-chome**  
**Isehara-shi, Kanagawa 259-11 (JP)**  
Inventor: **Watanabe, Isao**  
**34-6, Sagamidai 7-chome**  
**Sagamihara-shi, Kanagawa 228 (JP)**

(74) Representative: **Silverman, Warren et al**  
**HASELTINE LAKE & CO. Hazlitt House 28**  
**Southampton Buildings Chancery Lane**  
**London WC2A 1AT (GB)**

(54) Photosensitive, heat-resistant resin composition and pattern formation process.

(57) The film forming, photosensitive, heat-resistant resin composition comprising a varnish of a polyimide precursor having no photosensitivity in itself, a polymerizable monomer or oligomer compatible with said varnish and capable of providing a high-heat-resistant polymer upon being polymerized and a polymerization initiator for said monomer or oligomer. The resin composition is useful for the production of circuit substrates and semiconductor devices for high-density mounting including multi-chip modules or the like, such as printed circuits, printed boards, wiring boards and electronic components, can effectively avoid a reduction of the layer thickness during the film formation, and ensures a low cost production process. The pattern formation process using the same resin composition is also disclosed.

EP 0 453 237 A2



The present invention relates to a film forming, photosensitive, heat-resistant resin composition and a process for the formation of a heat-resistant insulating resin pattern. The film formed from the photosensitive, heat-resistant resin composition (in the present specification, the term "film" is used in a broad sense to indicate various coatings, films, thin films, etc.) has an excellent adhesion to the base material and a good heat resistance, moisture resistance, insulating properties, toughness, abrasion resistance, and weather resistance, and further, can be formed at a low cost. Further, the process for formation of a pattern according to the present invention is advantageous in that a photoresist for masking is not necessary, and a pattern of a heat-resistant insulating resin film formed by this process is useful as one component of a circuit board or a semiconductor device, and can be utilized, for example, as a protective film or an insulating film (layer insulating film) in printed circuits, printed boards, wiring boards, and electronic components for high-density mounting. The term "base material" or "base material to be treated" used in the present specification refers to mean general-use substrates including semiconductor substrates, ceramic substrates, metallic substrates, and various layered films and wiring.

Solder jointing is utilized for mounting IC chips in printed circuits, printed boards, wiring boards and electronic components including multi-chip modules or the like (as exemplified in Figs. 1 and 2) for high-density mounting, and accordingly, the insulating films used for the above-described circuit substrates should be able to withstand the heat applied during the soldering. Further, since a large amount of information must be rapidly processed, reductions in the size and increases in the volume of an information processor are required. Semiconductor devices constituting a major part of this processor have been integrated through a reduction in the size of unit elements, thus enabling LSIs and VLSIs to be put to practical use. The quantity of heat (heat value) emitted from the semiconductor device increases with an increase of the integration of unit elements, and in an LSI, the heat value amounts to about 10 W.

The integration is achieved by a multi-layerization of the circuit, and when forming a semiconductor integrated circuit element, an insulator is needed for a layer insulation and a surface protection, and inorganic insulators, such as phosphosilicate glass (abbreviated to "PSG"), silicon dioxide ( $\text{SiO}_2$ ) and silicon nitride ( $\text{Si}_3\text{N}_4$ ), are used for this purpose.

Although the above-described inorganic insulators have excellent properties such as a dielectric strength and heat resistance, it is difficult to form an insulating film having a large thickness because the insulating film is formed by a chemical vapor deposition process (abbreviated to "CVD").

The surface of a semiconductor substrate to be coated with an insulating film has a significant number of fine uneven portions having a large aspect ratio, and these inorganic insulating films are prepared in a film form similar to the form of the surface of the substrate, which raises the problems of an impossibility of smoothing the substrate surface and an insufficient coverage.

Accordingly, investigations have been made into the use of polyimide, which can be coated by the spin coating and has an excellent heat resistance, not only as a surface protective film of a semiconductor integrated circuit element but also as a layer insulating film. The polyimide film as a surface protective film or a layer insulating film can be formed by dissolving a polyimide precursor, such as bismaleimide, polyamide acid or diamine, in a solvent, such as N-methyl-2-pyrrolidone (abbreviated to "NMP"), coating the resulting solution on a semiconductor substrate by a method such as spin coating, and heating the coating to a temperature of 150 to 400°C to cause a cyclodehydration reaction, and thus cause the coating to be cured. The cyclodehydration reaction is also referred to as a polyimidalization reaction. Since the polyimide used herein has no photosensitivity in itself, a fine pattern of the polyimide has been formed by coating a photoresist on a polyimide precursor film, forming a resist pattern by photolithography, transferring the resist pattern to the lower layer by wet etching or plasma etching to form a pattern comprising a polyimide precursor, and heat-treating the pattern to cause a cyclodehydration reaction, to thereby form a polyimide pattern.

A polyimide having photosensitivity in itself, which enables a polyimide to be patterned to any form, has been developed and is commercially available from various manufacturers. In this photosensitive polyimide, a photosensitive functional group is introduced to in the molecule of a polyimide precursor, a photoreaction is conducted only in an exposed portion for polymerization, thereby varying the solubility between the unexposed portion and the exposed portion, and a development is then conducted by making use of a solvent to dissolve and remove the unexposed portion while leaving only the exposed portion.

In a subsequent heat treatment, a photosensitive group having a poor heat resistance is thermally decomposed and removed with the advance of a cyclodehydration, so that only a polyimide portion having good heat resistance remains as is. The photosensitive group can be introduced in the polyimide precursor through a covalent bond, an ionic bond or the like, and various photosensitive polyimides are commercially available.

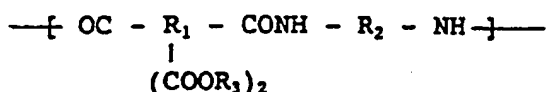
The use of the above-described photosensitive polyimide, however, has the problems of a high cost of the photosensitive polyimide per se, in addition to a large reduction of the film thickness due to the decomposition of a photosensitive group. Further, both the non-photosensitive polyimide and photosensitive polyimide have

the problem of a poor moisture resistance.

For reference, the following patents may be mentioned as an example of patents describing a process for the formation of a pattern.

Japanese Unexamined Patent Publication (Kokai) No. 56-22428 discloses a process for the formation of a polyimide pattern, characterized by comprising the steps of (1) forming a film of a photosensitive polyimide precursor on a substrate; (2) irradiating the film with light in a pattern form and conducting a development; (3) heating the developed polyimide precursor pattern to convert the pattern to a polyimide pattern; and (4) treating the resultant polyimide pattern with an etchant for polyimide. A polyimide precursor bonded to a photosensitive group through a chemical bond or mixed with a photosensitive compound (such as bichromate) is used as the photosensitive polyimide precursor. In this process, the development residue of the unexposed portion can be easily removed, so that a through-hole free from defects can be obtained.

Japanese Unexamined Patent Publication (Kokai) No. 59-107346 discloses a heat-resistant photosensitive material comprising a photosensitive polyimide precursor including structural units represented by the following formula:



wherein R<sub>1</sub> and R<sub>2</sub> are each an aromatic ring group, R<sub>3</sub> is a thietane ring, and COOR<sub>3</sub> is bonded to the amide group at its ortho-position. An insulating, heat-resistant polyimide pattern having a good adhesion to the semiconductor substrate can be prepared through the use of the photosensitive material in the formation of a pattern.

In addition to these Japanese Kokais, although it is not considered to be relevant to the present invention, Japanese Unexamined Patent Publication (Kokai) No. 54-109828 discloses a heat-resistant photoresist composition which comprises 100 parts by weight of at least one polymer selected from a variety of organic polar solvent-soluble, heat-resistant polymers including polyimide, and 0.1 to 100 parts by weight, preferably 1 to 50 parts by weight of a monomeric compound containing at least two ethylenically unsaturated double bonds in a molecule thereof. The amount of the monomeric compound incorporated into the heat-resistant polymer should not exceed 100 parts by weight, because such amount causes a reduction of the heat resistance of the resulting photoresist. This is because the selected monomeric compounds used herein do not exhibit an excellent heat resistance after curing of the resist.

The use of a photosensitive polyimide as a layer-insulating film in the production of an integrated circuit involving the generation of a considerable amount of heat during use is desired in the art. As described above, this photosensitive polyimide, however, has a problem of a lowering of the precision of a pattern due to a reduction in the film thickness through the decomposition of a photosensitive group in the step of heat-treating the photosensitive polyimide precursor to convert it into a polyimide, and further, a problem of a high cost of the material per se.

Accordingly, an object of the present invention is to provide a film forming, photosensitive, heat-resistant resin composition which is useful in the production of circuit substrates and semiconductor devices for high-density mounting including multi-chip modules or the like, such as printed circuits, printed boards, wiring boards and electronic components, causes no reduction in the film thickness during the formation of a film, and is low in cost.

Another object of the present invention is to provide an improved process for the formation of a pattern used for forming a heat-resistant insulating resin pattern through the use of the photosensitive, heat-resistant resin composition of the present invention, without the aid of a photoresist.

Still another object of the present invention is to provide a circuit board produced by using the above pattern formation process.

To attain these objects, the present inventors made intensive and extensive studies, and as a result, found that the use of a polyimide precursor having no photosensitivity in itself in combination with a particular polymerizable monomer or oligomer can eliminate the problems of the conventional photosensitive polyimide, and further, enables a polyimide film for use as a surface protective film or a layer-insulating film to be formed at a much lower cost than that of the conventional process.

According to one aspect of the present invention, there is provided a film forming, photosensitive, heat-resistant resin composition, characterized by comprising a varnish of a polyimide precursor having no photosensitivity in itself, a polymerizable monomer or oligomer compatible with said varnish and capable of providing a high-heat-resistant polymer upon being polymerized, and a polymerization initiator for said monomer or oligomer; and being designed for use in a polymerization process to first polymerize said monomer or oligomer

and simultaneously or subsequently cause a cyclodehydration reaction and cure (i.e. polymerize) said polyimide precursor through a heat treatment.

According to another aspect of the present invention, there is provided a process for the formation of a pattern, characterized by comprising the steps of: coating a base material to be treated, with a photosensitive, heat-resistant resin composition comprising a varnish of a polyimide precursor having no photosensitivity in itself, a polymerizable monomer or oligomer compatible with said varnish and capable of providing a high-heat-resistant polymer upon being polymerized, and a polymerization initiator for the monomer or oligomer; exposing the resultant coating of the photosensitive, heat-resistant resin composition to said conditions capable of inducing a polymerization of the polymerizable monomer or oligomer in a predetermined pattern, thereby selectively polymerizing the monomer or oligomer; selectively removing a region of the coating other than that where a polymer of the monomer or oligomer has been formed; and heat-treating the residual coating to cause a cyclodehydration reaction and cure the polyimide precursor contained in the coating.

According to another aspect of the present invention, there is provided a circuit board, which comprises a substrate and two or more electrically conductive layers applied over the substrate, the electrically conductive layer being insulated from each other through the upper and lower layer-insulating films, and being electrically connected with another electrically conductive layer through an interlayer conductor occupying a viahole in the layer-insulating film sandwiched therebetween, and in which the viahole-containing layer-insulating film is those prepared by the steps of:

coating an electrically conductive layer as a base material with a photosensitive, heat-resistant resin composition comprising a varnish of a polyimide precursor having no photosensitivity in itself, a polymerizable monomer or oligomer compatible with said varnish and capable of providing a high-heat-resistant polymer upon being polymerized and a polymerization initiator for said monomer or oligomer;

exposing the resultant coating of the photosensitive, heat-resistant resin composition to conditions capable of inducing a polymerization of said polymerizable monomer or oligomer in a predetermined pattern, thereby selectively polymerizing said monomer or oligomer;

selectively removing a region of said coating other than that where a polymer of said monomer or oligomer has been formed; and

heat-treating the residual coating to cause a cyclodehydration reaction and cure said polyimide precursor contained in the coating. The substrate used herein is preferably a member selected from the group consisting of a semiconductor substrate, a ceramic substrate, a metallic substrate, an inorganic substrate and an organic substrate.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made by way of example only to the accompanying drawings in which:

Fig. 1 is a perspective view showing one embodiment of the prior art multi-chip module to which the present invention is applicable;

Fig. 2 is a cross-sectional view of the multi-chip module of Fig. 1;

Fig. 3A to 3D are cross-sectional views showing, in sequence the pattern formation process of the present invention; and

Fig. 4A to 4C are schematic views showing, in sequence, the conversion of a polyimide precursor to polyimide.

In the present invention, a film forming, photosensitive, heat-resistant resin composition is prepared through a combination of a polyimide precursor having no photosensitivity in itself with, for example, an acrylic or methacrylic monomer or oligomer, a phosphazenic monomer or oligomer, other polymerizable monomer or oligomer and a polymerization initiator. The functions of the present invention will now be described by way of an embodiment, wherein the polymerizable monomer or oligomer is photopolymerizable.

As described above, the present inventors have studied a process which can eliminate the problems of the photosensitive polyimide, and further, can form a polyimide film for a layer-insulating layer at a much lower cost than that of the conventional process, and as a result have found that, when a base material to be treated is coated with a mixture of a photopolymerizable monomer or oligomer having an excellent heat resistance with a varnish of a polyimide precursor, subjected to selective exposure through the use of a mask or the like and developed, the varnish of the polyimide precursor in a non-exposed portion is dissolved and removed together with the monomer or oligomer while the varnish of the polyimide precursor in an exposed portion remains as it is together with a polymer derived from the monomer or oligomer.

When the varnish of the polyimide precursor and the polymer derived from the monomer or oligomer remaining in the exposed portion is then heat-treated, a cyclodehydration reaction of the polyimide precursor proceeds, thus causing the polyimide precursor to be converted into a polyimide. Nevertheless, since the polyimide resin pattern thus formed is a mixture or copolymer of a polyimide with the polymer of the monomer or oligomer, the heat resistance is inferior to that of a pattern consisting of a polyimide only. Note, said fact that

the polyimide resin pattern is a mixture or copolymer of a polyimide with the polymer is not that completely clarified, but it will be described hereinafter with reference to Figs. 4A to 4C. In this case, the use of a photopolymerizable monomer having an excellent heat resistance as the photopolymerizable monomer or oligomer enables the electrical properties required in electronic components, such as heat resistance and insulating properties, to be sufficiently maintained.

Specifically, in JIS (Japanese Industrial Standard) standards, the heat resistance during soldering at 270°C is specified as the heat resistance of electronic components, and the photosensitive, heat-resistant resin derived from the photosensitive, heat-resistant resin composition can sufficiently maintain the heat resistance specified in the JIS standards.

As a result of experiments, the present inventors found that the properties of the photosensitive, heat-resistant resin depend upon the properties of the photopolymerizable monomer or oligomer and photopolymerization initiator, rather than the varnish of a polyimide precursor.

In the practice of the present invention, any precursors of various polyimides (including modified products) can be used. According to the findings of the present inventors, the polyimide precursor may be prepared according to need or a commercially available one, and no significant difference is observed in the effect of these polyimides. A suitable polyimide precursor is a member selected from the group consisting of a precursor of a polyimide, a precursor of a modified polyimide, a precursor of a polybismaleimide and a precursor of a modified polybismaleimide. Similarly, polyimide engineering plastics also may be used. The above-described precursors may be used alone or in the form of a mixture thereof.

The polymerizable monomer or oligomer compatible with the varnish and capable of providing a high-heat-resistant polymer upon being polymerized is preferably an acrylic or methacrylic monomer or oligomer, and examples thereof include one having at least two functionalities in its molecule, one having an isocyanurate structure, one having an acryloyl or methacryloyl group in a terminal and/or a side chain in its molecule, an oligoester acrylate and a phosphazenic monomer or oligomer. The above-described polymerizable monomers or oligomers can be usually polymerized through the action of light, heat and the like, and photopolymerizable or heat polymerizable monomers or oligomers are preferred.

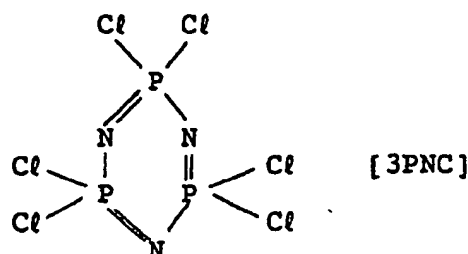
The present inventors have studied photopolymerizable monomers or oligomers having a good compatibility with the polyimide precursor and capable of providing a polymer having good heat resistance, and as a result, have found that acrylic or methacrylic monomers or oligomers which are commonly used as an ultraviolet curable adhesive are suitable.

Specifically, polyester acrylate, epoxy acrylate, urethane acrylate and silicone acrylate monomers or oligomers are useful as the acrylic or methacrylic monomer or oligomer. In particular, polyfunctional acrylate monomers or oligomers having an isocyanurate structure, for example, tris(acryloyloxyethyl) isocyanurate, isocyanuric acid EO ( $n = 3$ )- $\epsilon$ -caprolactone modified triacrylate, and branched polyfunctional acrylate monomers or oligomers, for example, trimethylolpropane triacrylate, EO-modified trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, and pentaerythritol hexaacrylate are useful. Further, methacrylic monomer or oligomer also can be similarly used, although a slight lowering in the photosensitivity is observed. In particular, it has been found that, when a lowering of the dielectric constant of the insulating film is intended, a blend of an acrylic or methacrylic fluoromonomer or fluorooligomer provides good results.

Further, the present inventors have found that inorganic polymer precursors used in the ultraviolet curable coating materials, especially phosphazenic monomers or oligomers and precursors (monomers or oligomers) of silicon-containing polymers also are suitable as the polymerizable monomer or oligomer.

The phosphazene compounds are known to be a coating material having good heat resistance (see Japanese Unexamined Patent Publication (Kokai) No. 63-241075). In the invention described in this publication, the phosphazene compounds are intended for use as a coating material for protecting the surface of decorative sheets, woods, plastics, paper, and clothes. For this reason, even if the phosphazene compound is used in a filler, the filler is limited to inorganic fillers and inorganic materials such as silica, and the disclosure is made regardless of the use of the phosphazene compound in combination with an organic material. Further, unlike the present invention, the above-described publication does not disclose applications whereby the phosphazene compound is combined with a polyimide precursor for use as a photosensitive insulating film which is selectively patterned in the same manner as that used in the photosensitive polyimide.

The phosphazenic monomer is preferably the following one wherein the chloro portion of the hexachloro-cyclo-triphenylphosphazene [3PNC] is substituted with, for example, an acrylate group, a methacrylate group, a vinyl group, or an allyl group.

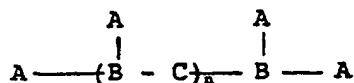


Specific examples thereof include a residue formed by removing a hydrogen atom from a hydroxyl group in methacrylates such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and 2-hydroxymethyl methacrylate (a hydroxyalkyl methacrylate residue), and a residue formed by removing a hydrogen atom from a hydroxyl group in acrylates such as 2-hydroxyethyl acrylate and 2-hydroxybutyl acrylate and 3-hydroxy-2-tert-butylpropyl acrylate (a hydroxyalkyl acrylate residue).

A residue formed by removing a hydrogen atom from a hydroxyl group in 2-hydroxyethyl methacrylate and a residue formed by removing a hydrogen atom from a hydroxyl group in 2-hydroxyethyl acrylate are particularly preferred. When the above-described various hydroxyalkyl methacrylate residues are compared with the hydroxyalkyl acrylate residues, the hydroxyalkyl acrylate residues are considered better because the crosslinking rate is higher. Further, the use in the form of a mixture with a polyfunctional acrylate or methacrylate monomer not containing any inorganic material is also possible.

Further, the present inventors have found that the following acrylic oligomers, which have been used as an ultraviolet curable adhesive, are also suitable as the polymerizable oligomer.

It has been found that oligomers or oligoester acrylates having a methacryloyl group in its terminal or side chain are especially useful as the acrylic oligomer. Except for special cases, an oligomer having an acryloyl group provide a higher reactivity and sensitivity than an oligomer having a methacryloyl group. More specifically, it has been found that trifunctional or higher functional acrylic oligomers having the following structure are particularly useful.



35 wherein

A is an acrylic acid, for example, acrylic acid or methacrylic acid;

B is a polyhydric alcohol, for example, 2-ethyl-2-hydroxymethyl-1,3-propanediol or pentaerythritol; and

C is a polybasic acid, for example, 3-cyclohexene-1, 2-dicarboxylic acid or 4-cyclohexene-1,2-dicarboxylic acid.

40 The polymerization of the polymerizable monomers or oligomers as listed above is induced and proceeds in the presence of a polymerization initiator through the action of light, heat or the like. Specifically, when the polymerization initiator is irradiated with light or heat, a radical is generated from the polymerization initiator and this radical induces the polymerization of the monomer or oligomer. The present inventors have made studies with a view to finding a polymerization initiator useful for the practice of the present invention, and as a result, have found that compounds well known to be capable of generating a radical through the action of light, for example, benzoin ether compounds, ketalin ether compounds, ketal compounds, acetophenone compounds, benzophenone compounds, thioxanthone compounds, organic peroxides, N-phenylglycine, triazine compounds and allene-iron complexes, are suitable. Typical examples of the polymerization initiator are as follows, but it should be understood that the polymerization initiator is not limited to these only.

50 Benzoin ether compounds:

isopropyl benzoin ether, isobutyl benzoin ether, etc.

Ketal compounds:

1-hydroxycyclohexyl phenyl ketone, benzyl dimethyl ketal, etc.

Acetophenone compounds:

55 acetophenone, 2-hydroxy-2-methylpropiophenone, 4-isopropyl-2-hydroxy-2-methylpropiophenone, etc.

Benzophenone compounds:

benzophenone, methyl o-benzoylbenzoate, etc.

Thioxanthone compounds:

2-methylthioxanthone, 2-chlorothioxanthone, etc.

Organic peroxides:

ketone peroxide, peroxy ketal, hydroperoxide, dialkyl peroxide, diacyl peroxide, peroxy ester, peroxy dicarbonate, etc.

5 Triazine compounds:

Compounds having a 1,3,5-triazine structure and at least one trichloromethyl group in its molecule, such as 2,4,6-tris(trichloromethyl)-1,3,5-triazine and 2,4-bis(trichloromethyl)-6-phenyl-1,3,5-triazine.

Allene-iron complexes:

( $\eta^6$ -benzene) ( $\eta^5$ -cyclopentadienyl) iron (II) hexafluorophosphate, ( $\eta^6$ -pyrene) ( $\eta^5$ -cyclopentadienyl) iron (II) hexafluoroantimonate, ( $\eta^6$ -naphthalene) ( $\eta^5$ -cyclopentadienyl) iron (II) hexafluorophosphate, etc.

The above-described polymerization initiators may be used alone or in the form of a mixture thereof. Further, it is possible to enhance the sensitivity through exposure at an optimal wavelength.

Further, the use of the above-described polymerization initiator in combination with a sensitizer is recommended from the viewpoint of the effect. Examples of suitable sensitizer include di-n-butylamine, n-butylamine, 15 triethylamine and triethylenetetramine and further ketocoumarin dyes, coumarin dyes, thioxanthene dyes, xanthene dyes and thioerythrin salt dyes.

In the photosensitive, heat-resistant resin composition according to the present invention, mixing proportions of the polyimide precursor, polymerizable monomer or oligomer and polymerization initiator may be widely varied depending upon factors such as desired results. The present inventors have found that the above-described acrylic monomer or oligomer in an amount of 10 to 500% by weight based on the polyimide precursor (weight of the polyimide precursor contained in the varnish) and the polymerization initiator in an amount of 0.1 to 50% by weight based on the monomer or oligomer are useful. Since the polymerizable monomer or oligomer is more inexpensive than the polyimide precursor, the cost of the resultant photosensitive, heat-resistant resin film or a pattern per se formed therefrom drops with an increase of the amount of addition of the monomer or oligomer. Further, the photosensitivity is increased with an increase of the amount of addition of the monomer or oligomer and photopolymerization initiator.

The formation of the heat-resistant, insulating resin pattern according to the present invention starts with the coating of the photosensitive, heat-resistant resin composition on the base material to be treated. The coating is conducted by uniformly applying a resin composition in the form of a photosensitive liquid or the like on the surface of a selected base material, for example, a ceramic substrate, such as alumina ( $Al_2O_3$ ), or a metallic substrate, a semiconductor substrate (for example, a silicon substrate or a sapphire substrate) or the like in the case of use as circuit substrates, printed boards and wiring boards for high-density mounting including multi-chip module by the conventional coating process, such as spin coating, dip coating or doctor blade coating. The coating of the photosensitive, heat-resistant resin composition thus formed is prebaked at a properly elevated temperature to evaporate to some extent a solvent contained therein (the varnish of the polyimide precursor usually contains 80% by weight or more of N-methyl-2-pyrrolidone as a solvent).

After the prebaking, the resultant coating is exposed to conditions capable of inducing a polymerization of the polymerizable monomer or oligomer in a predetermined pattern (corresponding to a pattern of an intended heat-resistant, insulating resin film). Preferably, a pattern of light necessary for generating a radical from the simultaneously used polymerization initiator is applied to the coating, or a pattern of heat necessary for generating such a radical is applied to the coating. Specifically, a selective irradiation with light, such as ultraviolet, is conducted through a mask. Consequently, only the polymerizable monomer or oligomer contained in the exposed portion (or heated portion) is selectively polymerized.

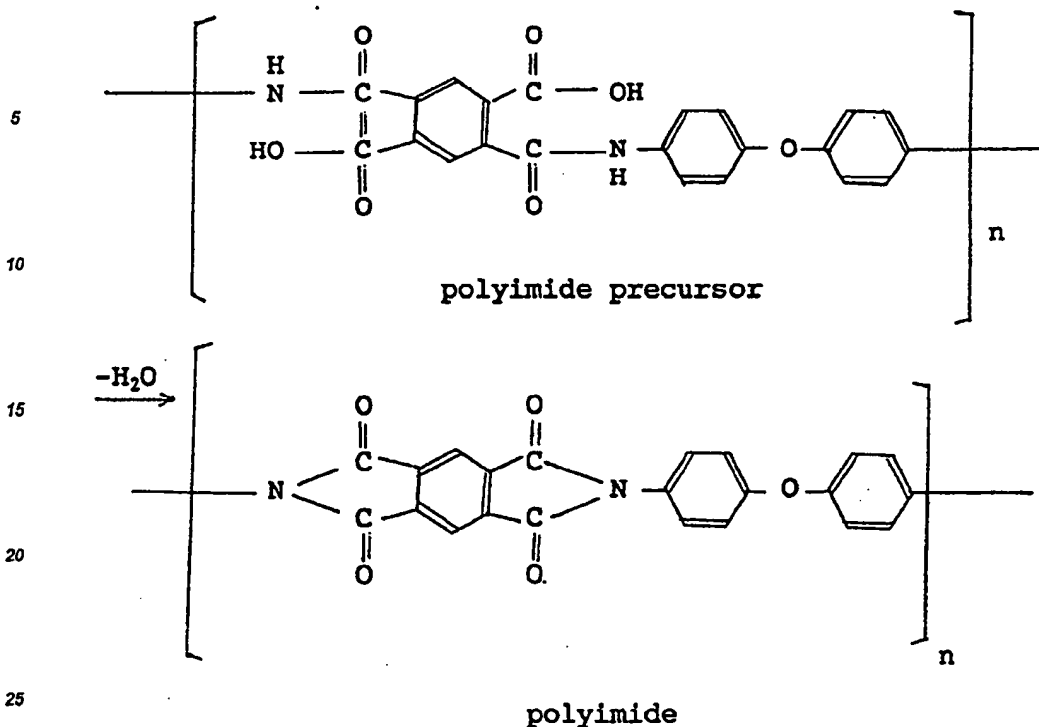
Then, in the coating, the region other than that where a polymer has been formed from the monomer or oligomer is selectively removed. A development wherein use is made of a developing solution comprising a solvent capable of dissolving the polyimide precursor and polymerizable monomer or oligomer can be advantageously conducted for the above-described removal.

Subsequently, the coating remaining undissolved and unremoved in the development is heat-treated to polymerize the polyimide precursor in the coating. The heat treatment temperature (heating temperature) in this step is not particularly limited as long as the polyimide precursor is converted into a polyimide without decomposition of the polymerizable monomer or oligomer. In general, however, the temperature is preferably about 250 to 350°C.

According to the process of the present invention, a pattern of a heat-resistant, insulating resin having satisfactory properties can be obtained at a low cost through the above-described series of steps. Further, it is also advantageously possible to form an unpatterned photosensitive, heat-resistant resin film through the use of this process.

As described above, the present invention can be advantageously used for the production of multi-chip module. An embodiment of the multi-chip module is shown in Figs. 1 (appearance) and Fig. 2 (cross-section).





For a further understanding of the present invention, the photosensitive, heat-resistant resin composition according to the present invention and the formation of a pattern using the same will now be described by way of the following Examples.

#### Example 1

In the present Example, the use of various polyimide precursors will be described.

Varnish of polyimide precursor: (precursor content  
of varnish: 14.5% by weight) ... 50.0 g

photopolymerizable monomer: [tris(acryloyloxyethyl)  
isocyanurate] ... 10.0 g

photopolymerization initiator: benzophenone  
... 1.0 g

Varnish of polyimide precursor and varnish of a polybismaleimide precursor each having a precursor (14.5% by weight) were prepared, and a significant difference between precursors was examined with the same monomer and photopolymerization initiator.

A photosensitive solution having the above-described composition was spin-coated on a pretreated Si wafer having a diameter of 3 in., and the coated wafer was prebaked at 90°C for 1 hr. The thickness of the film after the prebaking was 5 μm.

A negative type glass mask having a minimum pattern width of 30 μm was provided on the photosensitive plate and irradiated with an ultraviolet of a wavelength of 250 nm under condition of an exposure of 480 mJ/cm<sup>2</sup>.

Then, the photosensitive plate was subjected to an ultrasonic wave development with N-methyl-2-pyrrolidone and rinsed in ethyl alcohol, thereby developing the plate. The unexposed region was eluted or dissolved while leaving the exposed pattern region only.

Specifically, the multi-chip module shown in the drawings is provided with LSI chip 2 mounted on a substrate 1 and further a flexible printed board 3. Further, as shown in Fig. 2, this multi-chip module has a layer structure such that, for example, a layer-insulating film 11 of the present invention, a grounding layer 12, a signal layer 13, an electric power supply layer 14 and a surface electrode layer 15 are successively laminated on a substrate 10, such as a silicon wafer or a ceramic substrate. An interlayer conductor 16 is filled in viaholes of interconnecting the upper and lower conductive layers.

Generally speaking, the multi-chip modules to which the present invention can be applied have a minimum size of approximately 5 cm x 5 cm and include, for example, silicon (Si) wafer having a diameter of 3 in. or plate such as glass, aluminum, copper or ceramic plate, having a size of approximately 70 mm x 70 mm. A pattern of the electrical conductor body such as aluminum or copper can be formed at varied layer thicknesses and pattern widths. The conductor pattern can be formed, for example, by vapor depositing a conductor metal followed by selectively wet etching the deposited metal. Photolithographic process is preferably used in this wet etching. The interlayer insulator or layer-insulating film of the present invention, made of the described heat-resistant composition, can be applied at a film thickness of less than 40  $\mu\text{m}$ .

In this connection, the pattern formation process of the present invention will be described with reference to Figs. 3A to 3D and Figs. 4A to 4C.

A photosensitive solution or resin composition of the present invention is spin-coated on a Si wafer having a diameter of 3 in., and then prebaked at 90°C for 1 hr. As illustrated in Fig. 3A, a film 21 of the resin composition having a thickness of 5  $\mu\text{m}$  is formed on the Si wafer 20. As shown in Fig. 4A, the film of the resin composition comprises the photopolymerizable monomer (or oligomer) 26 and polyimide precursor 27.

Next, as illustrated in Fig. 3B, a negative type glass mask 25 having a pattern width of 20  $\mu\text{m}$  is disposed over the Si wafer 20, and the film 21 of the resin composition is exposed through the glass mask 25 to an ultraviolet having a wavelength of about 250 nm (or radiation having a wavelength of 250 to 400 nm from a Hg lamp) at an exposure level of 480 mJ/cm<sup>2</sup>. As a result of this selective exposure, the unexposed area of the film 21 is not changed, but the exposed area 22 is changed because the photopolymerizable monomer was polymerized with the irradiation of ultraviolet. Namely, as shown in Fig. 4B, the exposed area 22 comprises polyimide precursor 27 and polymerization product 28 of the monomer (or oligomer) in addition to the unreacted monomer (or oligomer) (not shown).

After selective exposure, the film 21 is developed with a solution of N-methyl-2-pyrrolidone by using an ultrasonic development. As illustrated in Fig. 3C, the exposed area 22 remains on the wafer 20.

Finally, the wafer 20 is heated at 270°C for 30 min (or at a suitable temperature of 250 to 350°C for suitable time) to convert the polyimide precursor to polyimide. As illustrated in Fig. 3D, a pattern 23 of the resulting polyimide resin is obtained on the wafer 20. The resulting polyimide resin is shown in Fig. 4C. Namely, the polyimide resin comprises the polymerization product 28 of the monomer (or oligomer) and polyimide 29. Note, Figs. 4A to 4C are schematic views, and therefore the forms and proportions of the components 26, 27, 28 and 29 are illustrated to assist in the understanding of the conversion of polyimide precursor to polyimide resin.

The conversion of polyimide precursor to polyimide resin is represented by the following reaction schema:

The plate was then heated at 270°C for 30 min to convert the residual polyimide precursor into a polyimide resin. As a result, although the depth of the yellow color of the pattern region the slightly increased, no other change was observed.

The pattern was observed under a microscope, and no breakage was found in any sample. The thermal decomposition temperature of the resin in the pattern region was measured, and it was found that the resins were stable up to about 350°C, regardless of the types of varnish used as the precursor.

### Example 2

In the present invention, the use of various photopolymerizable monomers will be described.

An experiment was conducted in the same manner as that of Example 1, except that the kind of varnish of the polyimide precursor and the photopolymerization initiator were fixed as described in the above-described Example 1 with the use of four varied photopolymerizable monomers as given below and the photosensitive plates were irradiated with ultraviolet having a wavelength of 250 nm in suitable exposures.

The kind of the photopolymerizable monomer, exposure and thermal decomposition temperature are given in Table 1. The kind and amount of addition of the photopolymerizable monomer were indicated by Nos. 1 to 5 (No. 1 is the same material as that used in Example 1).

No. 1: tris(acryloyloxyethyl) isocyanurate (amount of addition: 10 g)

No. 2: glycidyl acrylate (amount of addition: 5 g)

No. 3: pentaerythritol triacrylate (amount of addition: 20 g)

No. 4: dipentaerythritol hexaacrylate (amount of addition: 15 g)

No. 5: mixture of tris(acryloyloxyethyl) isocyanurate (amount of addition: 6 g) with trimethylolpropane triacrylate (amount of addition: 4 g)

The patterns were observed under a microscope, and no breakage was found in any sample. The thermal decomposition temperature of the resin in the pattern region was measured, and as a result, the heat resistance was 280 to 400°C in terms of the thermal decomposition temperature.

Table 1

Photopolymerizable monomer	Exposure (mJ/cm <sup>2</sup> )	Decomposition temp. (°C)
No. 1	480	350
No. 2	960	400
No. 3	400	280
No. 4	640	300
No. 5	560	320

### Example 3

In the present Example, the use of various photopolymerization Initiators will be described.

An experiment was conducted in the same manner as that of Example 1, except that the kind of varnish of the polyimide precursor and the photopolymerizable initiator were fixed as described in the above-described Example 1 with the use of six varied photopolymerization initiators as given below and the photosensitive plates were irradiated with ultraviolet having a wavelength of 250 nm in suitable exposures.

The kind of the photopolymerization initiator and the exposure necessary for the formation of a pattern are given in Table 2. The kind and amount of addition of the photopolymerization initiator were indicated by Nos. 1 to 6 (No. 1 is benzophenone, i.e., the same material as that used in Example 1).

No. 1: benzophenone (amount of addition: 1.0 g)

No. 2: 3,3'-4,4'-tetra-(tert-butylperoxycarbonyl) benzophenone (amount of addition: 0.80 g)

No. 3: isopropyl benzoin ether (amount of addition: 2.0 g)

No. 4: 2-hydroxy-methyl-propiophenone (amount of addition: 0.50 g)

No. 5: 2-methylthioxanthone (amount of addition: 0.20 g)

No. 6: 2,4-bis(trichloromethyl)-6-phenyl-1,3,5-triazine (amount of addition: 1.50 g)

The patterns were observed under a microscope, and no breakage was found in any sample.

These results are those obtained when the development was conducted in the same developing condition as that of the above-described Example 1, and are not equal to the sensitivity of the photopolymerization initiator. Therefore, it has been found that the sensitivity varies with a varying of the amount of addition of the photopolymerization initiator and the developing condition.

Table 2

Photopolymerization initiator	Exposure (mJ/cm <sup>2</sup> )
No. 1	480
No. 2	400
No. 3	400
No. 4	800
No. 5	1,280
No. 6	560

#### Example 4

In the present Example, the use of a modified polyimide precursor will be described.

varnish of polyimide precursor: silicone-modified  
polyimide (precursor content of  
varnish: 13.5% by weight)  
..... 50.0 g  
photopolymerizable monomer: pentaerythritol  
tetraacrylate ..... 12.0 g  
photopolymerization initiator: benzoyl peroxide  
..... 2.0 g

A photosensitive solution having the above-described composition was spin-coated on a pretreated Si wafer having a diameter of 3 in., and the coated wafer was prebaked at 120°C for 1 hr. The thickness of the film after the prebaking was 6 μm.

A negative type glass mask having a minimum pattern width of 30 μm was provided on the photosensitive plate and irradiated with a high-pressure mercury lamp for 20 sec.

Then, the photosensitive plate was subjected to an ultrasonic wave development with a mixed solution comprising N-methyl-2-pyrrolidone and methyl cellosolve and rinsed in isopropyl alcohol, thereby developing the plate. The unexposed region was eluted while leaving the exposed pattern region only.

The plate was then heated at 300°C for 30 min to convert the residual polyimide precursor into a polyimide resin, and as a result, although the depth of yellow color of the pattern region was slightly increased, no other change was observed.

The pattern was observed under a microscope, and no breakage was found in any sample. The thermal decomposition temperature of the resin in the pattern region was measured, and it was found that the resins were stable up to about 300°C.

Example 5

varnish of polyimide precursor: polyimide precursor  
(14.5% by weight)

..... 50.0 g

phosphazene monomer: HEMA6-substituted 3PNC (3PNC  
in which each of six (6)  
Chlorine substituents is  
substituted with 2-hydroxyethyl  
methacrylate) ..... 10.0 g

photopolymerization initiator:  
2,2-dimethoxy-2-  
phenylacetophenone ... 1.00 g

solvent: methyl ethyl ketone ..... 10.0 g

A photosensitive solution having the above-described composition was spin-coated on a pretreated Si wafer having a diameter of 3 in., and the coated wafer was prebaked at 90°C for 1 hr. The thickness of the film after the prebaking was 3  $\mu$ m.

A negative type glass mask having a minimum pattern width of 30  $\mu$ m was provided on the photosensitive plate and irradiated with an ultraviolet from a high-pressure mercury lamp (wavelength: 250 - 400 nm) in an exposure of 500 mJ/cm<sup>2</sup> (in terms of a wavelength of 365 nm).

Then, the photosensitive plate was subjected to an ultrasonic wave development with N-methyl-2-pyrrolidone and rinsed in ethyl alcohol, thereby developing the plate. The unexposed region was eluted while leaving the exposed pattern region only.

The pattern region was then heated at 260°C for 30 min to convert the residual polyimide precursor into a polyimide resin, and as a result, although the depth of yellow color of the pattern region was slightly increased, no other change was observed.

The pattern was observed under a microscope, and no breakage was found. The thermal decomposition temperature of the resin in the pattern region was measured, and the resins were found to be stable up to about 350°C.

Example 6 to 8

Patterns were formed in the same manner as that of the above-described Example 5, except that HEMA6-substituted 3PNC (3PNC in which each of six Cl substituents is substituted with 2-hydroxyethyl acrylate), a mixture of HEMA6-substituted 3PNC with trimethylolpropane triacrylate or a mixture of HEMA6-substituted 3PNC with pentaerythritol triacrylate and isocyanuric acid EO-modified ( $n = 3$ ) triacrylate was used instead of HEMA6-substituted 3PNC used in the above-described Example 5. In the observation of the appearance under a microscope, no abnormal portion was found. The thermal decomposition temperature of the resin in the pattern region was measured. The results are given in the following Table 3.

Table 3

Ex.No.	Monomer	Exposure (mJ/cm <sup>2</sup> )	Thermal decom- position temp. (°C)
5	HEMA6-substituted 3PNC (10.0 g)	500	350
6	HEA6-substituted 3PNC (6.0 g)	750	400
7	HEMA6-substituted 3PNC (8.0 g) + trimethylol- propane triacrylate (4.0 g)	350	330
8	HEMA6-substituted 3PNC (5.0 g) + pentaerythritol triacrylate (5.0 g) + isocyanuric acid EO- modified (n = 3) triacrylate (5.0 g)	400	360

Example 9 to 13

Exposures suitable for the formation of a pattern were examined in the same manner as that of the above-described Example 5, except that 3,3'-4,4'-tetra-(tert-butylperoxycarbonyl) benzophenone, isopropyl benzoin ether, 2-hydroxy-2-methyl-propiophenone, 2-methylthioxanthone or 2,4-bis(trichloromethyl)-6-phenyl-1,3,5-triazine was used instead of 2,2-dimethoxy-2-phenylacetophenone. The results are given in Table 4. These results are those obtained when the development was conducted in the same developing condition as that of the above-described Example 5 and do not completely equal the sensitivity of the photopolymerization initiator. It also has been found that the sensitivity varies with a varying of the amount of addition of the photopolymerization initiator and the developing condition.

Table 4

Ex.No.	Photopolymerization initiator	Exposure (mJ/cm <sup>2</sup> )
5	2,2-dimethoxy-2-phenylacetophenone (1.00 g)	500
9	3,3'-4,4'-tetra-(tert-butylperoxy- carbonyl) benzophenone (0.80 g)	250
10	isopropyl benzoin ether (2.00 g)	400
11	2-hydroxy-2-methyl-propiophenone (0.50 g)	800
12	2-methylthioxanthone (0.20 g)	1,000
13	2,4-bis(trichloromethyl)-6-phenyl- 1,3,5-triazine (1.50 g)	350

## Example 14

varnish of silicone-modified polyimide precursor:

silicone-modified polyimide  
precursor (13.5% by weight)

..... 50.0 g

phosphazene monomer: HEA6-substituted 3PNC (3PNC

in which each of six Cl

substituents is substituted with

2-hydroxyethyl acrylate)

..... 12.0 g

photopolymerization initiator: benzoyl peroxide

..... 2.00 g

A photosensitive solution having the above-described composition was spin-coated on a glass substrate having a size of 70 x 70 x 1 mm, and the coated substrate was prebaked at 120°C for 1 hr. The thickness of the film after the prebaking was 5 μm.

A negative type glass mask having a minimum pattern width of 30 μm was provided on the photosensitive plate and irradiated with a high-pressure mercury lamp for 60 sec.

Then, the photosensitive plate was subjected to an ultrasonic wave development with a mixed solution comprising

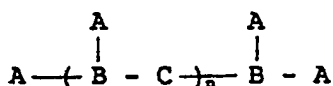
N-methyl-2-pyrrolidone and methyl cellosolve and then rinsed in isopropyl alcohol, thereby developing the plate. The unexposed region was eluted while leaving the exposed pattern region only.

The pattern region was then heated at 250°C for 50 min to convert the residual polyimide precursor into a polyimide resin, and as a result, although the depth of yellow color of the pattern region was slightly increased, no other change was observed.

The pattern was observed under a microscope, and no breakage was found. The thermal decomposition temperature of the resin in the pattern region was measured, and as a result, the resin was found to be stable up to about 300°C.

Example 15

varnish of polyimide precursor: polyimide precursor  
 (14.5% by weight) ..... 50.0 g  
 acrylic oligomer: oligomer ① represented by the  
 following formula ..... 10.0 g



wherein

A: acrylic acid

B: 2-ethyl-2-hydroxymethyl-1,3-propanediol

C: 3-cyclohexene-1,2-dicarboxylic acid

: 4-cyclohexene-1,2-dicarboxylic acid photopolymerization Initiator: 2,2-dimethoxy-2-phenylacetophenone ..... 1.00 g

A photosensitive solution having the above-described composition was spin-coated on a silicon wafer having a diameter of 3 in., and the coated wafer was prebaked at 120°C for 1 hr. The thickness of the film after the prebaking was 9 µm.

A negative type glass mask having a minimum pattern width of 30 µm was provided on the photosensitive plate and irradiated with ultraviolet by means of an ultraviolet exposing machine at an exposure of 600 mJ/cm<sup>2</sup> (365 nm).

Then, the photosensitive plate was subjected to an ultrasonic wave development with N-methyl-2-pyrrolidone and then rinsed in ethyl alcohol, thereby developing the plate. The unexposed region was eluted while leaving the exposed pattern region only.

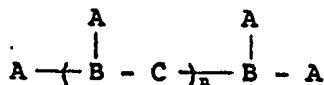
The pattern region was then heated at 300°C for 30 min to convert the residual polyimide precursor into a polyimide resin. As a result, although the depth of yellow color of the pattern region was slightly increased, no other change was observed.

The pattern was observed under a microscope, and no breakage was found. The thermal decomposition temperature of the resin in the pattern region was measured, and as a result, the resin was found to be stable up to about 350°C.

Example 16 to 20

Patterns were formed in the same manner as that of the above-described Example 15, except that the following oligomer 2, oligomer 3, mixture of oligomer 1 with pentaerythritol triacrylate, mixture of oligomer 2 with trimethylolpropane triacrylate and mixture of oligomer 3 with isocyanuric acid EO-modified (n = 3) triacrylate were used instead of acrylic oligomer 1 used in the above-described Example 15. The appearance of the patterns was observed under a microscope, and no breakage was found. The thermal decomposition temperature of the resin in the pattern region was measured. The results are given in Table 5.

acrylic oligomer ②:



wherein

A: methacrylic acid

B: 2-ethyl-2-hydroxymethyl-1,3-propanediol

C: 4-cyclohexene-1,2-dicarboxylic acid

acrylic oligomer ③:



Table 6

Ex.No.	Photopolymerization initiator	Exposure (mJ/cm <sup>2</sup> )
15	2,2-dimethoxy-2-phenylacetophenone (1.00 g)	600
21	3,3'-4,4'-tetra-(tert-butylperoxy- carbonyl) benzophenone (0.80 g)	540
22	isopropyl benzoin ether (2.00 g)	840
23	benzyl dimethyl ketal (0.50 g)	960
24	2-methylthioxanthone (0.20 g)	1,200
25	2,4,6-tris(trichloromethyl)- 1,3,5-triazine (1.50 g)	720
26	benzoyl peroxide (1.50 g)	840
27	2,4-bis(trichloromethyl)-6-phenyl- 1,3,5-triazine (0.50 g)	1,200
28	( $\eta^6$ -benzene) ( $\eta^5$ -cyclopentadienyl)- (II) hexafluorophosphate (2.00 g)	720
29	N-phenylglycine (1.80 g)	840

Example 30

varnish of silicone-modified polyamide precursor:  
silicone-modified polyamide precursor  
(13.5% by weight) ..... 50.0 g  
acrylic oligomer: oligomer 1 ..... 5.0 g  
monomer: isocyanuric acid EO (n = 3)· $\epsilon$ -caprolactone  
modified triacrylate ..... 5.0 g  
photopolymerization initiator: 2-hydroxy-2-methyl-  
propiophenone ..... 1.50 g

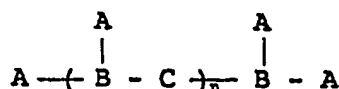
A photosensitive solution having the above-described composition was spin-coated on a pretreated Si wafer having a diameter of 3 in., and the coated wafer was prebaked at 100°C for 1 hr. The thickness of the film after the prebaking was 8  $\mu$ m.

A negative type glass mask having a minimum pattern width of 30  $\mu$ m was provided on the photosensitive plate and irradiated with a high-pressure mercury lamp for 40 sec.

Then, the photosensitive plate was subjected to an ultrasonic wave development with a mixed solution comprising N-methyl-2-pyrrolidone and methyl cellosolve and then rinsed in isopropyl alcohol, thereby developing the plate. The unexposed region was eluted while leaving the exposed pattern region only.

The pattern region was then heated at 280°C for 30 min to convert the residual polyimide precursor into a polyimide resin. As a result, although the depth of yellow color of the pattern region was slightly increased, no other change was observed.

The pattern was observed under a microscope, and no breakage was found. The thermal decomposition



wherein

A: acrylic acid

B: 2-ethyl-2-hydroxymethyl-1,3-propanediol

: pentaerythritol

C: 3-cyclohexene-1,2-dicarboxylic acid

: 4-cyclohexene-1,2-dicarboxylic acid

Table 5

Ex.No.	Oligomer	Exposure (mJ/cm <sup>2</sup> )	Thermal decom- position temp. (°C)
15	oligomer ① (10.0 g)	600	350
16	oligomer ② ( 5.0 g)	960	400
17	oligomer ③ (15.0 g)	600	330
18	oligomer ① ( 6.0 g) + pentaerythritol triacylate ( 6.0 g)	720	300
19	oligomer ② ( 6.0 g) + trimethylolpropane triacylate ( 4.0 g)	840	360
20	oligomer ③ ( 5.0 g) + isocyanuric acid EO- modified (n = 3) triacylate ( 8.0 g)	800	340

Example 21 to 29

Exposures necessary for the formation of a pattern were determined in the same manner as that of Example 15, except that 3,3'-4,4'-tetra-(tert-butylperoxycarbonyl) benzophenone, isobutyl benzoin ether, benzyl methyl ketal, 2-methylthioxanthone, 2,4,6-tris(trichloromethyl)-1,3,5-triazine, benzoyl peroxide, 2,4-bis(trichloromethyl)-6-phenyl-1,3,5-triazine, ( $\eta^6$ -benzene) ( $\eta^5$ -cyclopentadienyl) (II) hexafluorophosphate and N-phenylglycine were used instead of 2,2-dimethoxy-2-phenylacetophenone used in the above-described Example 15. The results are given in Table 6. These results are those obtained when the development was conducted in the same developing condition as that of the above-described Example 15 and do not completely equal the sensitivity of the photopolymerization initiator. It also has been found that the sensitivity varies with a varying of the amount of addition of the photopolymerization initiator and the developing condition.

temperature of the resin in the pattern region was measured, and as a result, the resin was found to be stable up to about 330°C.

#### Example 31

5

Viaholes were formed by the use of a photosensitive solution having the same composition as that of the above-described Example 30 in the same manner as that of the Example 30, except that a pretreated ceramic substrate ( $\text{Al}_2\text{O}_3$ ) having a bell size, a pretreated glass substrate having a size of 70 x 70 x 1 mm, a pretreated aluminum plate having a size of 70 x 70 x 2 mm and a pretreated copper plate having a size of 70 x 70 x 1 mm were used instead of the 3 in. diameter Si wafer and use was made of a negative type glass mask having a minimum viahole size of 50  $\mu\text{m}\phi$ . In the observation under a microscope after curing, it has been found that via-holes having a size up to 50  $\mu\text{m}\phi$  were formed.

As can be appreciated from the above description, a photosensitive, heat-resistant resin can be provided at a low cost through the practice of the present invention. This resin has not only a heat resistance sufficient for use as layer insulating films, surface protective films or the like for circuit substrates, printed boards and wiring boards for high-density mounting including multi-chip modules or the like but also a heat resistance above a soldering temperature and further, as opposed to the conventional process, brings no reduction in the film thickness caused by the photosensitive group, which makes it possible to form a pattern having a high dimensional accuracy.

Further, according to the present invention, it is possible to provide a useful heat-resistant insulating film which is superior to the conventional insulating film in the adhesion to the base material and has a good moisture resistance, excellent various properties inherent in the inorganic high-molecular materials, such as phosphazene compounds, including hardness, abrasion resistance and chemical resistance, a photosensitivity, a heat resistance above the soldering temperature and a considerably lower cost than that of the polyimide resin. Other effects of the present invention can be easily understood from the above detailed description of the invention.

#### Claims

30

1. A film forming, photosensitive, heat-resistant composition, characterised by comprising a varnish of polyimide precursor having no photosensitivity in itself, a polymerizable monomer or oligomer compatible with said varnish and capable of providing a high-heat-resistant polymer upon being polymerized and a polymerization initiator for said monomer or oligomer.

35

2. A photosensitive, heat-resistant resin composition according to claim 1, in which said polyimide precursor is a precursor of a polyimide, a precursor of a modified polyimide, a precursor of a polybismaleimide or a precursor of a modified polybismaleimide.

40

3. A photosensitive, heat-resistant resin composition according to claim 1 or 2, in which said polymerizable monomer or oligomer is an acrylic or methacrylic monomer or oligomer.

4. A photosensitive, heat-resistant resin composition according to claim 1, 2 or 3, in which said monomer or oligomer has at least two functional groups in its molecule.

45

5. A photosensitive, heat-resistant resin composition according to claim 1 or 2, in which said polymerizable monomer or oligomer is a monomer or oligomer having an isocyanurate structure.

50

6. A photosensitive, heat-resistant resin composition according to claim 1 or 2, in which said polymerizable monomer or oligomer is a phosphazenic monomer or oligomer.

7. A photosensitive, heat-resistant resin composition according to claim 1 or 2, in which said polymerizable monomer or oligomer is a mixture of an acrylic or methacrylic monomer or oligomer with a phosphazenic monomer or oligomer.

55

8. A photosensitive, heat resistant resin composition according to claim 3, 4 or 7, in which said acrylic monomer or oligomer is a monomer or oligomer having an acryloyl or methacryloyl group at a terminal and/or a side chain in its molecule.

9. A photosensitive, heat-resistant resin composition according to claim 3, 4 or 7, in which said acrylic monomer or oligomer is an oligoester acrylate.
10. A photosensitive, heat-resistant resin composition according to any preceding claim, in which said polymerization initiator is a benzoin ether compound, a ketal compound, an acetophenone compound, a benzophenone compound, a thioxanthone compound, an organic peroxide, a N-phenylglycine, a triazine compound or an allene-iron complex.
11. A process for formation of a pattern, which comprises the steps of:
- coating a base material to be treated with a photosensitive, heat-resistant resin composition as claimed in any preceding claim;
  - exposing the resultant coating of the photosensitive, heat-resistant resin composition to conditions capable of inducing a polymerization of said polymerizable monomer or oligomer in a predetermined pattern, thereby selectively polymerizing said monomer or oligomer;
  - selectively removing a region of said coating other than that where a polymer of said monomer or oligomer has been formed; and
  - heat-treating the residual coating to cause a cyclodehydration reaction and cure said polyimide precursor contained in the coating.
12. A process for formation of a pattern according to claim 11, in which said polymerization initiator is a photopolymerization initiator and the coating of said photosensitive, heat-resistant resin composition is exposed to a light pattern to induce and advance a polymerization of said polymerizable monomer or oligomer through the action of a radical generated from said photopolymerization initiator.
13. A process for formation of a pattern according to claim 11, in which said polymerization initiator is a heat polymerization initiator and the coating of said photosensitive, heat-resistant resin composition is pattern-wise heated to induce and advance a polymerization of said polymerizable monomer or oligomer through the action of a radical generated from said heat polymerization initiator.
14. A process for formation of a pattern according to any one of claims 11 to 13, which is used for production of circuit substrates for high-density mounting including printed circuits, printed boards, wiring boards and electronic components.
15. A circuit board, which comprises a substrate and two or more electrically conductive layers applied over the substrate, the electrically conductive layer being insulated from each other through the upper and lower layer-insulating films, and being electrically connected with another electrically conductive layer through an interlayer conductor occupying a viahole in the layer-insulating film sandwiched therebetween, and in which the viahole-containing layer-insulating film has been prepared by the steps of:
- coating an electrically conductive layer as a base material with a photosensitive, heat-resistant resin composition as claimed in any one of claims 1 to 10;
  - exposing the resultant coating of the photosensitive, heat-resistant resin composition to conditions capable of inducing a polymerization of said polymerizable monomer or oligomer in a predetermined pattern, thereby selectively polymerizing said monomer or oligomer;
  - selectively removing a region of said coating other than that where a polymer of said monomer or oligomer has been formed; and
  - heat-treating the residual coating to cause a cyclodehydration reaction and cure said polyimide precursor contained in the coating.
16. A circuit board according to claim 15, in which the substrate is a semiconductor substrate, a ceramic substrate, a metallic substrate, an inorganic substrate or an organic substrate.

Fig. 1

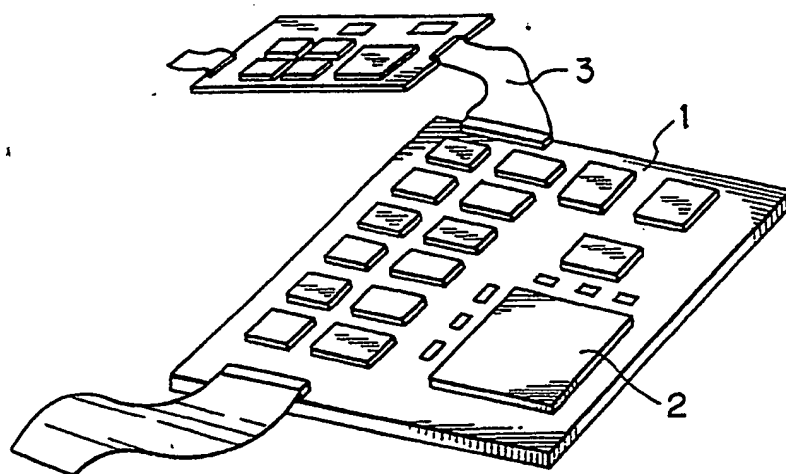


Fig. 2

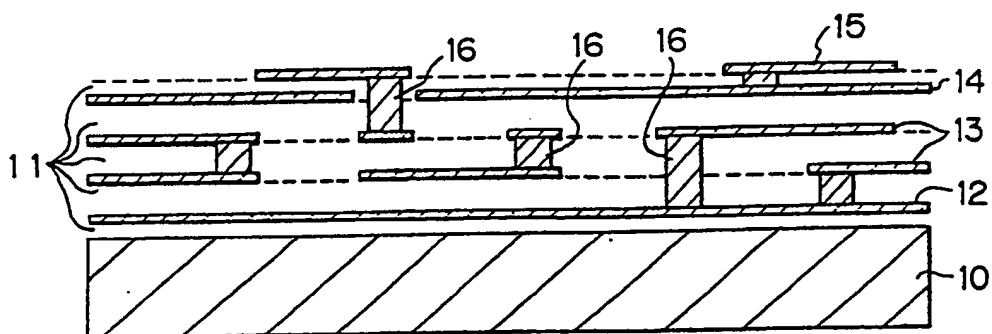


Fig. 3A

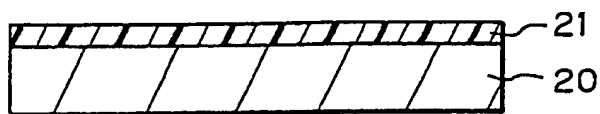


Fig. 3B

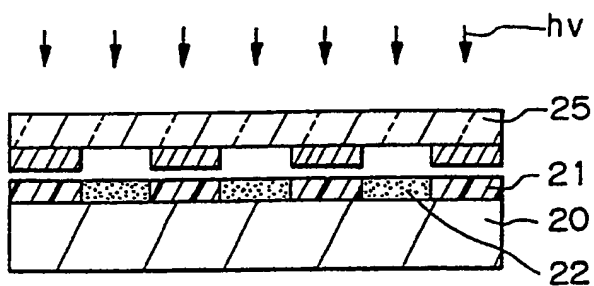


Fig. 3C

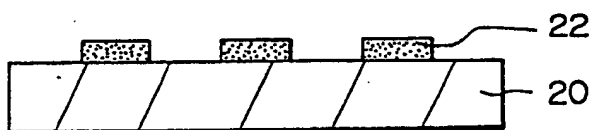
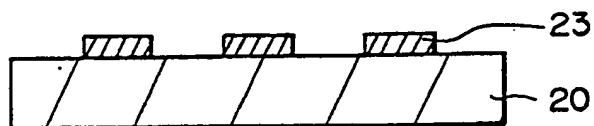
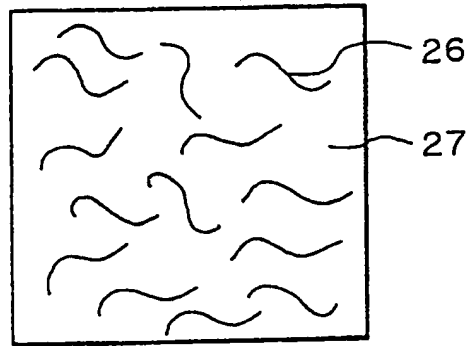


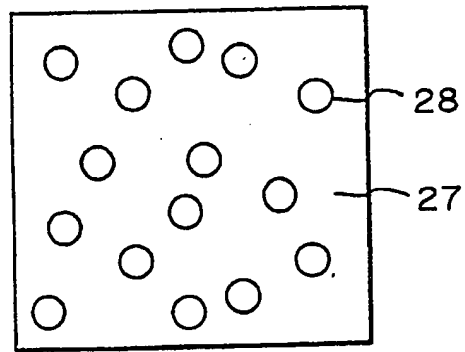
Fig. 3D



*Fig. 4A*



*Fig. 4B*



*Fig. 4C*

